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13. ABSTRACT (Maximum 200 words) It is well known that the electrostrictive response of all materials is small at low applied electric fields. However, the electrostrictive strains(S) are related to the square of the applied field(E). It therefore appeared reasonable to assume that for a soft polymeric material, a large thickness response, d_T ($d_T = \frac{\partial S}{\partial E}$), might be obtained by application of sufficiently high D.C. bias fields(~20MV/m) to a film while driving the film with an A.C. signal. Under such high electric fields, d_T values greater than 3 Å/V were obtained for a low crystallinity poly(vinylidene fluoride) (PVF ₂) film containing 65% by weight of a plasticizer tricresyl phosphate (TCP). Values of 6 Å/V were obtained for certain classes of thermoplastic elastomers, i.e., polyurethanes. These values are considerably greater than those obtained from conventional piezoelectric ceramic materials and an order of magnitude greater than the 0.25 Å/V obtained from polarized PVF ₂ . In addition, large elastic strains (>3%) were observed as a function of applied D.C. field.					
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ELECTROSTRICTIVE RESPONSE OF ELASTOMERIC POLYMERS

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Abstract: It is well known that the electrostrictive response of all materials is small at low applied electric fields. However, the electrostrictive strains(S) are related to the square of the applied field(E). It therefore appeared reasonable to assume that for a soft polymeric material, a large thickness response, d_T ($d_T = \frac{\partial S}{\partial E}$), might be obtained by application of sufficiently high D.C. bias fields($\sim 20\text{MV/m}$) to a film while driving the film with an A.C. signal. Under such high electric fields, d_T values greater than 3 \AA/V were obtained for a low crystallinity poly(vinylidene fluoride) (PVF_2) film containing 65% by weight of a plasticizer tricresyl phosphate (TCP). Values of 6 \AA/V were obtained for certain classes of thermoplastic elastomers, i.e., polyurethanes. These values are considerably greater than those obtained from conventional piezoelectric ceramic materials and an order of magnitude greater than the 0.25 \AA/V obtained from polarized PVF_2 . In addition, large elastic strains ($>3\%$) were observed as a function of applied D.C. field.

Results and Discussion

Over the past several years we have investigated the effects of the addition of plasticizers, including tricresyl phosphate (TCP) on the ferroelectric, piezoelectric and pyroelectric properties of poly(vinylidene fluoride) (PVF₂)^(1,2) and its copolymers. These polymers constituted the only class of ferroelectric semicrystalline polymers known, until our recent discovery of the ferroelectric nature of the odd-numbered nylons, such as Nylon 11, Nylon 9, Nylon 7 and Nylon 5^(3,4). We have shown that the addition of TCP to PVF₂ before polarization of the films results in a decrease in the coercive electric field (switching field), an increase in the remanent polarization, and significant enhancement of the piezoelectric and pyroelectric response^(1,5). In addition, the presence of TCP as a plasticizer significantly modifies the elastic modulus and dielectric constant of the polarized films⁽²⁾. This, of course, permits a tailoring of the electromechanical properties (mechanical modulus and dielectric constant) of the films for application purposes.

Our work has also shown that the TCP resides in the amorphous regions of this semicrystalline polymer, so that the addition of large amounts of plasticizer results in a decrease in crystallinity, i.e., the plasticizer acts as a solvent. After this study, we began to examine the possibility of obtaining oriented crystallization of PVF₂ from a TCP solution under high electric fields⁽⁶⁾. A solution of PVF₂ in TCP was placed onto a copper electrode, with the second electrode placed over this rubbery gel-like solution. This sandwich was placed in a high vacuum unit, and the TCP was slowly evaporated at high temperature while an applied electric field was increased to match the increasing dielectric strength of the solution. The PVF₂ crystals grew in the phase I crystal form (the most polar phase) with

preferred (dipole) orientation, (i.e., b-axis) in the applied field direction. The modulus, dielectric constant and piezoelectric and pyroelectric response of the crystallized films were found to be a function of the TCP content remaining (another method for obtaining tailored electromechanical properties). In addition, the solution grown oriented phase I crystals were stable to their melting point.

As a consequence of these studies, we were approached by a government agency (DARPA) to consider development of a new class of PVF₂-based piezoelectric polymers having a modulus of 10⁷ N/m² to 10⁸ N/m² (the modulus of PVF₂ being ~ 10⁹ N/m²) and a piezoelectric thickness coefficient d_T ~ 5 Å/Volt (the thickness coefficient of PVF₂ normally being ~ 0.2 Å/V). The thickness coefficient, d_T, is defined as the derivative of the strain(S) with respect to the applied electric field(E):

$$d_T = \frac{\partial S}{\partial E} = d_{(E=0)} + 2ME \quad (1)$$

where M is the electrostrictive coefficient. This request constituted a contradiction in that to achieve the appropriate modulus, the amount of TCP required decreased the film crystallinity to below 10% and resulted in a greatly decreased value of thickness coefficient. This, of course, resulted from the fact that ~80% of the polar crystals responsible for the piezoelectric activity were no longer present.

Given two contradictory requirements, we looked for alternative methods to achieve the required properties. It was apparent that no piezoelectric material, polymeric or otherwise, would satisfy these property requirements, and this led us to consider the possibility of using the electrostrictive response of a polymer. It is well known that the electrostrictive response of soft polymeric materials is small at low applied electric fields.

However, our studies of the crystallization of PVF₂ from solution under high electric field had demonstrated that rubbery samples of PVF₂ with high TCP content could be subjected to electric fields as high as ~ 100 MV/m. The dielectric strength (value of electric field at sample breakdown) of such a polymer/plasticizer system depends principally upon the conducting impurities present, since both PVF₂ and TCP are excellent insulators. Because electrostrictive strains are related to the square of the applied field ($S=dE+ME^2$), where d is a piezoelectric coefficient, and given our knowledge of the magnitude of the high electric fields which can be applied, it occurred to us that a large thickness response might be obtained by application of a high D.C. bias field, while driving the polymer film with an A.C. signal as shown schematically in Figure 1.

Films of PVF₂, heavily plasticized with TCP to achieve an elastic modulus between 10^7 N/m² and 10^8 N/m², were prepared and sent to BBN (Cambridge, Massachusetts) for measurement. These films exhibited the response we expected, as shown in Fig. 2. At the highest fields, the data showed some scatter, but values of d_T approaching 4 Å/volt were observed. The initial plasticizer content of 65% by weight made the samples difficult to measure accurately, since plasticizer extruded from the system during the measurement process; however, the feasibility of the idea had been established.

To avoid the difficulties encountered in dealing with a polymer/plasticizer system, we decided to explore a different class of polymers, the thermoplastic elastomers, which can have the required elastic modulus without use of plasticizers. We anticipated that some degree of polarity would be important to mimic the PVF₂/plasticizer system, and decided to investigate the polyurethanes and the polyureas. The first films were prepared using a urethane resin.

The film was driven with a 10V peak to peak AC signal, while subjected to a range of applied bias fields. The apparatus used for measurement was based on the BBN design used for the initial measurements and is shown schematically in Fig. 3. The data obtained is shown in Fig. 4, with d_T saturating at values of $\sim 6 \text{ \AA/V}$.

The liquid-like nature of a thermoplastic elastomer such as polyurethane, with an elastic modulus of $\sim 10^7 \text{ N/m}^2$ and a value of Poisson's Ratio of $\sim 1/2$, suggested that a constraint of film lateral displacement by the measurement apparatus electrodes (see Figure 3) during thickness change might produce a value of d_T considerably less than that of a free film, and that the values measured might be significantly lower than those obtained from an unconstrained film. Investigations of this possibility are being conducted and will be reported in the future.

We then placed the polyurethane film sample in the arrangement shown in Fig. 5, where the sample thickness determined the distance between the plates of an air gap capacitor. By measuring the change in air-gap capacitance, we were able to measure the static thickness strains as a function of applied bias field. The results are shown in Fig. 6. The strains obtained at the highest fields applied are very large ($>3\%$) and exhibit hysteresis like behavior.

Application of these materials in electroacoustic devices, actuators, and possibly artificial muscles is quite apparent. Doubtless, many other applications of this novel phenomenon will occur over time.

Acknowledgment

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References and Notes

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Figure Captions

Fig. 1: Schematic diagram of electrostrictive response curve.

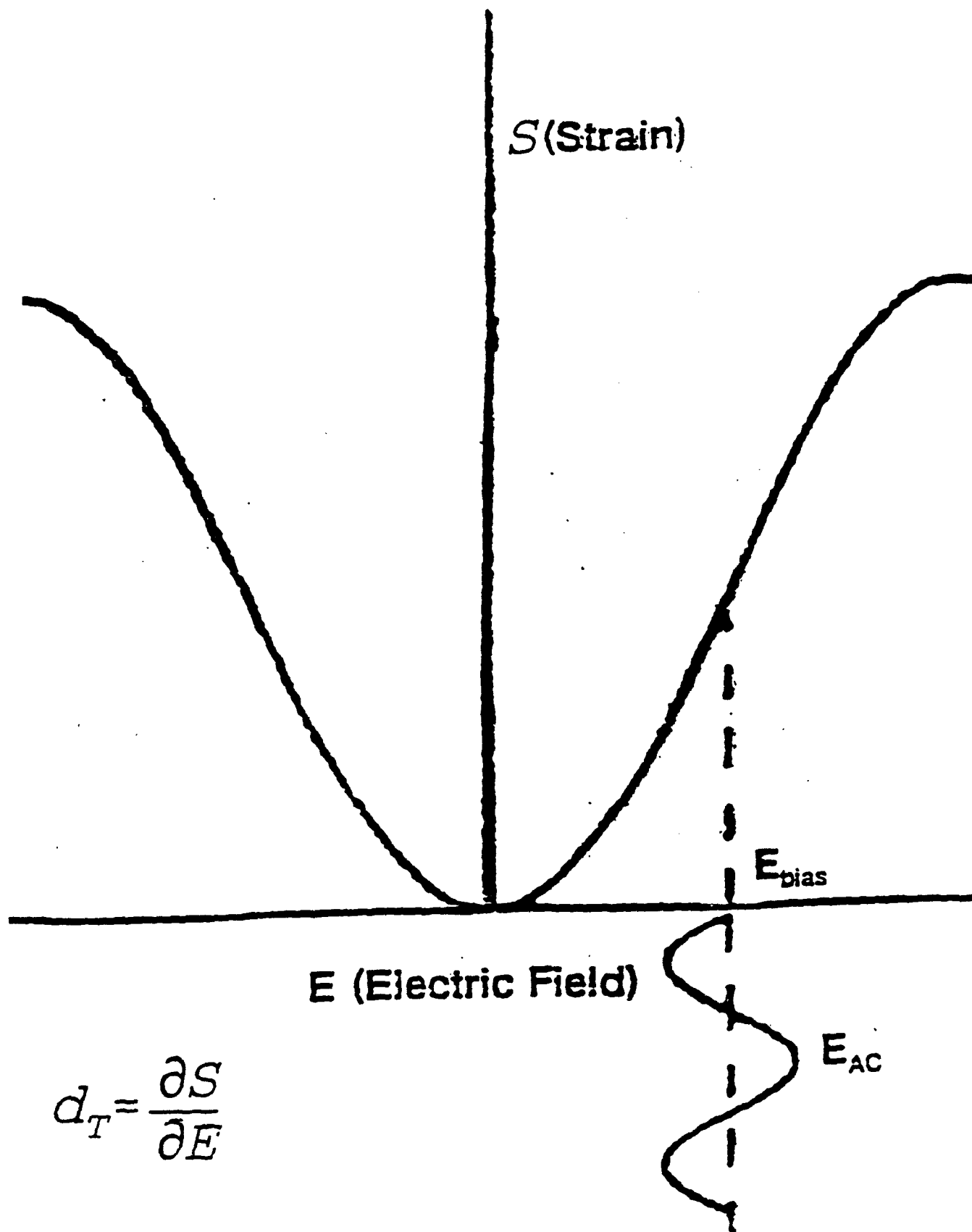
Fig. 2: Variation of thickness coefficient (d_T) with applied bias field for a plasticized (65%) polyvinylidene fluoride (PVF₂) film.

Fig. 3: Schematic diagram of apparatus used to measure the thickness coefficient d_T .

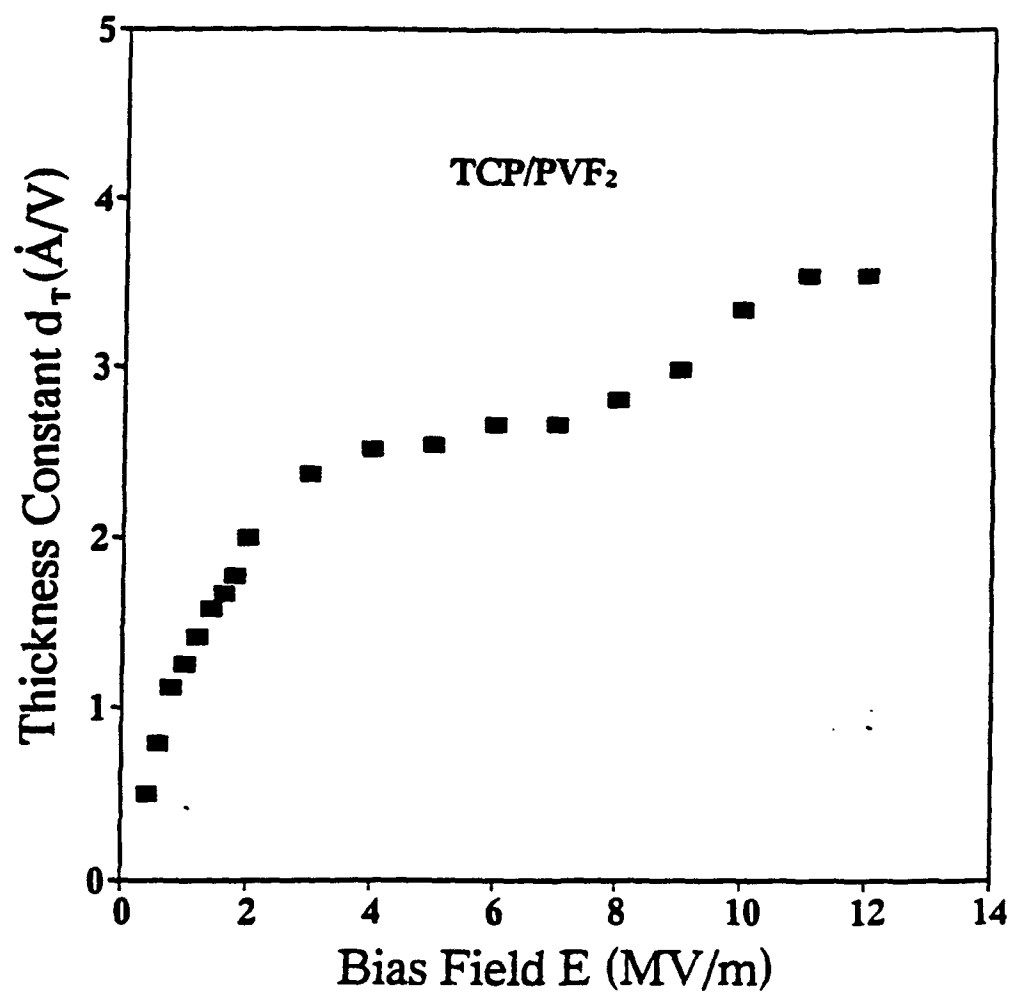
Fig. 4: Variation of thickness coefficient (d_T) with an applied bias field for a polyurethane thermoplastic elastomer.

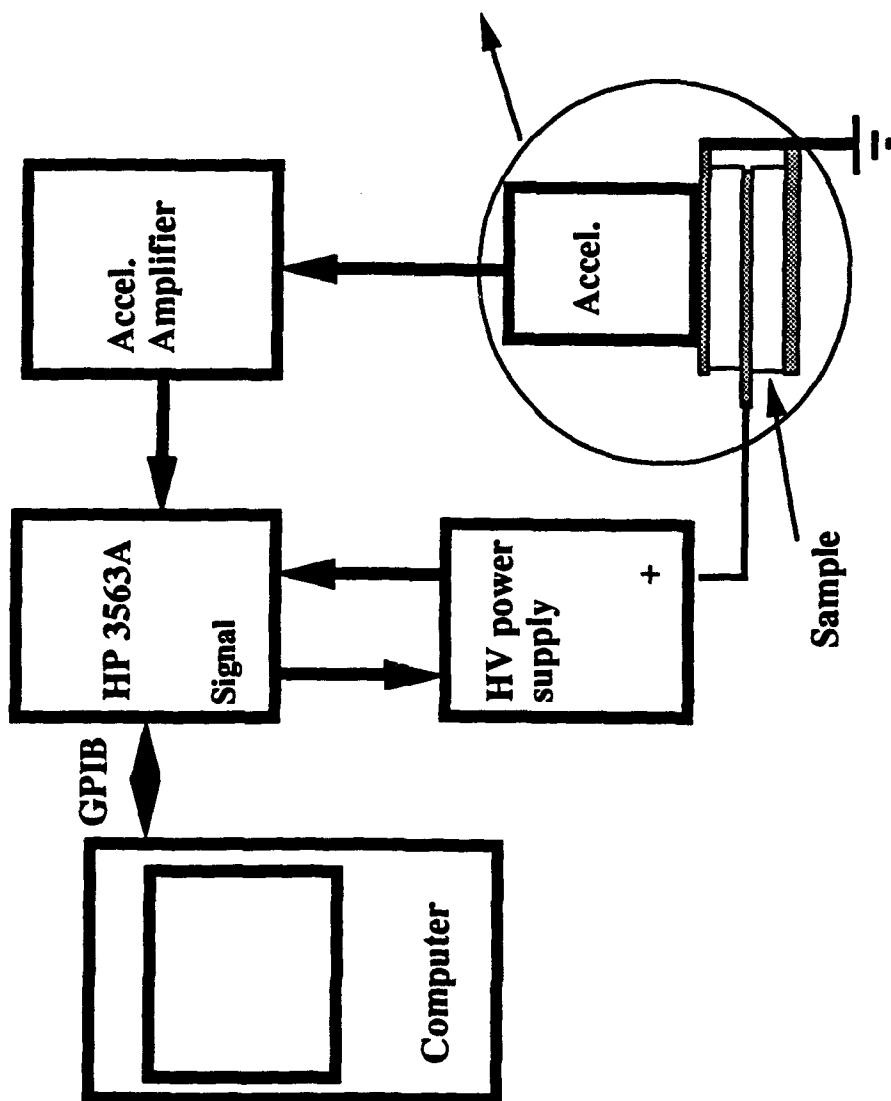
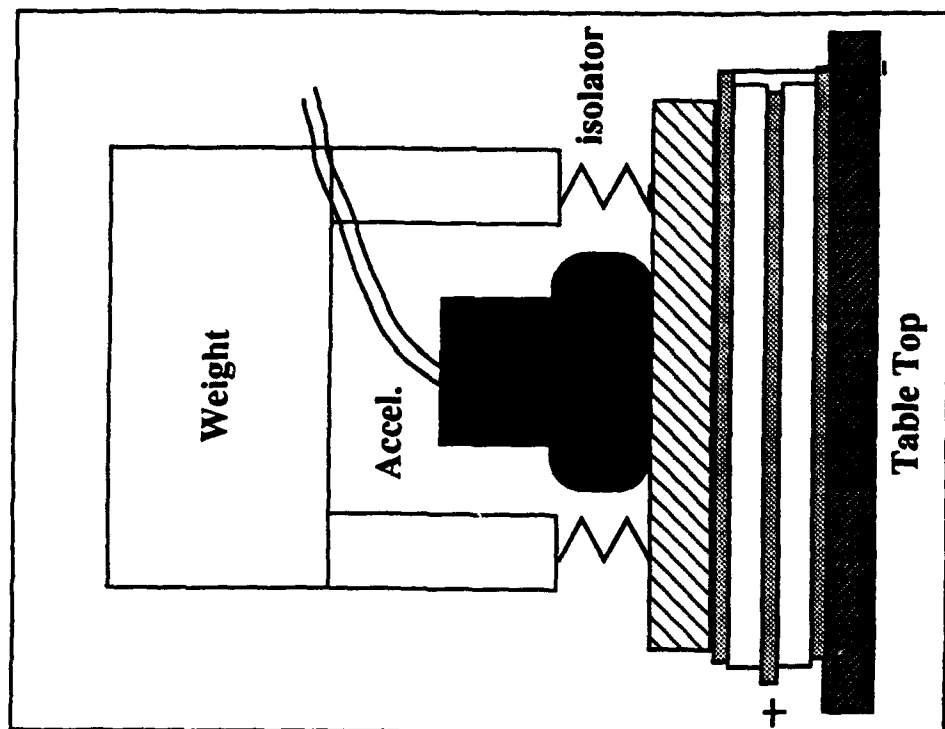
Fig. 5: Schematic diagram of apparatus used to measure the static thickness change as a function of applied bias field.

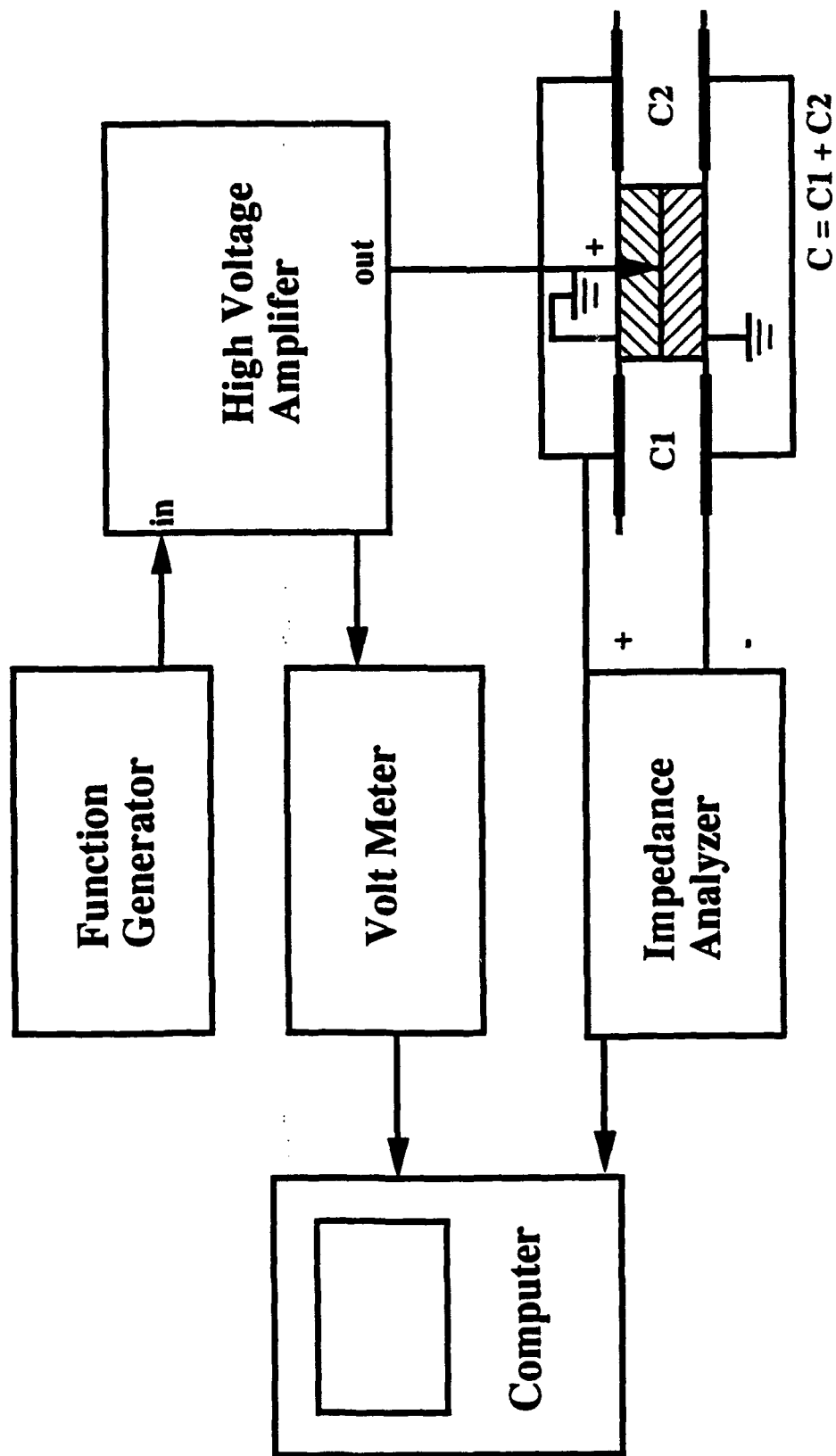
Fig. 6: Variation of static electrostrictive strains with applied bias field.

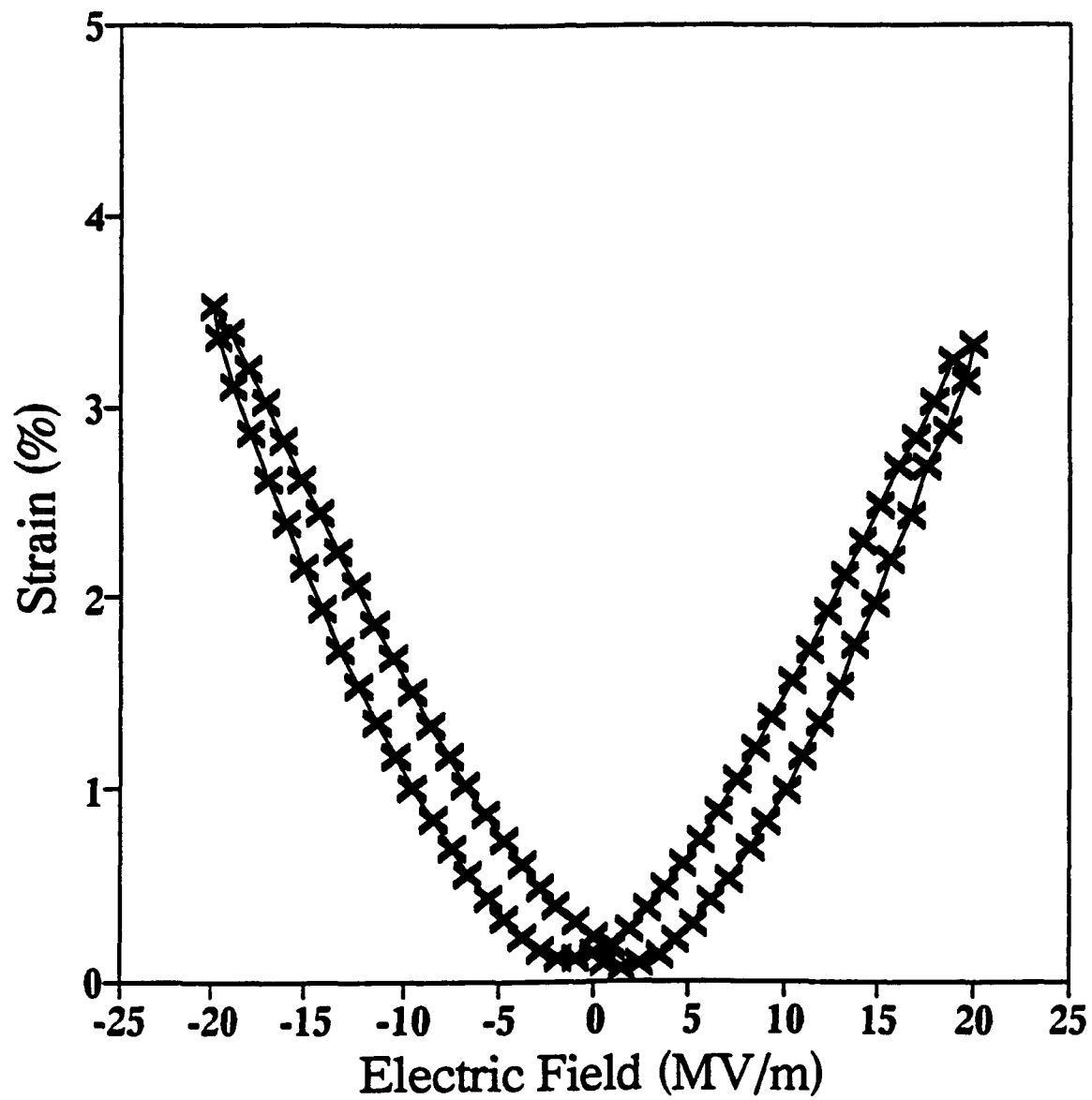


$$d_T = \frac{\partial S}{\partial E}$$









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